

N92-22460

HIGH TEMPERATURE ADHESIVES

Terry L. St. Clair, Head
Polymeric Materials Branch
NASA Langley Research Center
Hampton, VA 23665-5225

ABSTRACT

The aerospace and electronics industries have an ever increasing need for higher performance materials. In recent years linear aromatic polyimides have been proven to be a superior class of materials for various applications in these industries. The use of this class of polymers as adhesives is continuing to increase. Several NASA Langley-developed polyimides show considerable promise as adhesives because of their high glass transition temperatures, thermal stability, resistance to solvents/water, and their potential for cost-effective manufacture.

INTRODUCTION

Over the past 2 decades several commercially attractive polyimide adhesives have been developed at the NASA Langley Research Center [1-4]. These materials were developed as structural adhesives for use in the 200-300°C range, however they appear to have utility for other end-use applications. One particular adhesive, LARC-TPI (Langley Research Center Thermoplastic Polyimide), has become commercially available. Three other linear thermoplastic polyimides have been developed in more recent years that exhibit characteristics that for one reason or another have made them candidates for scaleup by NASA. They are LARC-CPI (Crystalline Polyimide), LARC-ITPI (Isomeric TPI) and LARC-IA (Improved Adhesive). Their properties will be discussed.

LARC-CPI

This semicrystalline poly(keto-ether-imide) can be readily processed above its crystalline melt temperature (343°C) to form adhesive bonds of very high strength [2]. The structure of this polyimide as well as the other three mentioned in the introduction are shown in Figure 1. After the bonding operation, the adhesive crystallizes upon cool down and can continue to crystallize during thermal exposures near the glass transition temperature of the polymer (223°C). Figure 2 illustrates this behavior. The adhesive performance of LARC-CPI is shown in Figure 3. The tendency of this adhesive to gain strength when aged at 232°C and tested at this same temperature is attributed to the development of crystallinity.

The resistance to organic solvents and to base hydrolysis that is exhibited by LARC-CPI is evidently due to the crystallinity. In 20 percent sodium hydroxide solution, LARC-CPI shows no tendency to hydrolyze even after a week period. This is a phenomenal property that allows this material to be used in some very hostile environments that would totally hydrolyze just about all other polyimides. LARC-CPI, again because of its crystallinity, has an extremely low level of water pickup (less than 0.5 percent).

LARC-ITPI

LARC-ITPI was developed as a cost effective alternative to LARC-TPI. A major drawback to the large scale commercialization of LARC-TPI has been associated with its cost which is primarily caused by the diamine component, 3,3'-diaminobenzophenone. The diamine that is used in LARC-ITPI is the very reasonably priced meta-phenylenediamine (MPD). The adhesive performance of LARC-ITPI is shown in Figure 4. The IDPA-MPD is the LARC-ITPI with two versions being represented. The center set of bar graphs represents the controlled molecular weight form of the polymer which has four percent endcap (EC 4.00). Its adhesive performance is quite comparable to LARC-TPI. Their glass transition temperatures are similar (258°C and 260°C). These two adhesives exhibit very similar properties after 1000 hours of exposure at 232°C.

LARC-IA

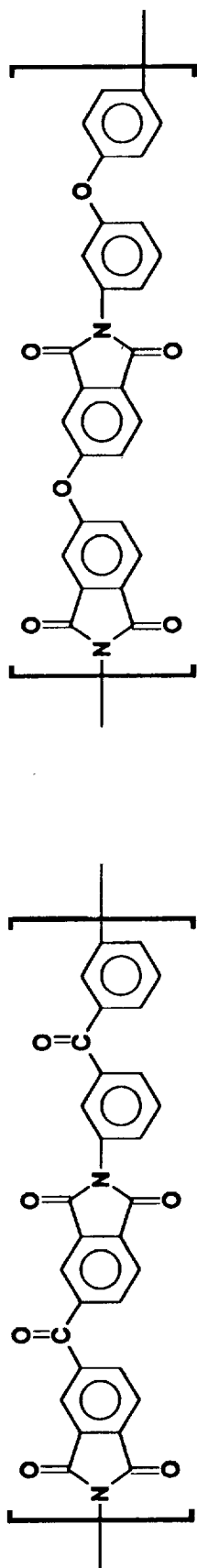
LARC-IA is the designation for the polyimide based on the novel diamine 3,4'-oxidianiline (3,4'-ODA). This diamine became available due to the development of a novel high tensile-strength, high-modulus polyamide in Japan. The use of this diamine in a BTDA-based polyimide resulted in an adhesive with a glass transition temperature of 243°C. Just as with the LARC-ITPI it was necessary to control the molecular weight this time with five percent endcapper (phthalic anhydride). Some selected adhesive properties of LARC-IA are shown in Figures 5 and 6. In these Figures LARC-IA is compared with and without aluminum powder which improves its high temperature performance.

SUMMARY

Several high temperature polymers have been developed at NASA Langley Research Center that have been shown to exhibit exceptional adhesive properties. The four systems that have been investigated the most are the commercially available LARC-TPI and the three experimental systems designated LARC-CPI, LARC-ITPI and LARC-IA. Each of these materials has special attractive properties which make them commercially attractive.

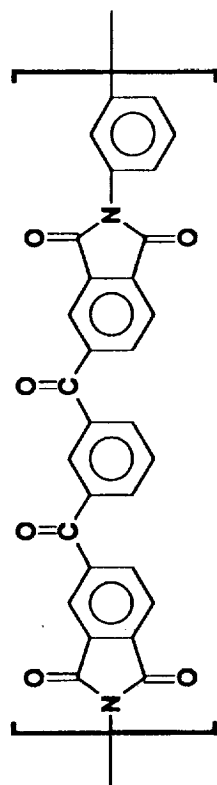
REFERENCES

1. St. Clair, A. K. and St. Clair, T. L., SAMPE Quarterly, **13**(1), pp. 20-25 (1981).
2. Hergenrother, P. M. and Havens, S. J., Inter. SAMPE Symp., **36**, pp. 56-63 (1991).
3. Pratt, J. R.; St. Clair, T. L. and Progar, D. J., U.S. Patent 4,937,317, June 1990.
4. Progar, D. J. and St. Clair, T. L., J. Adhesion Sci. Technology, **4**(7), pp. 527-549 (1990).

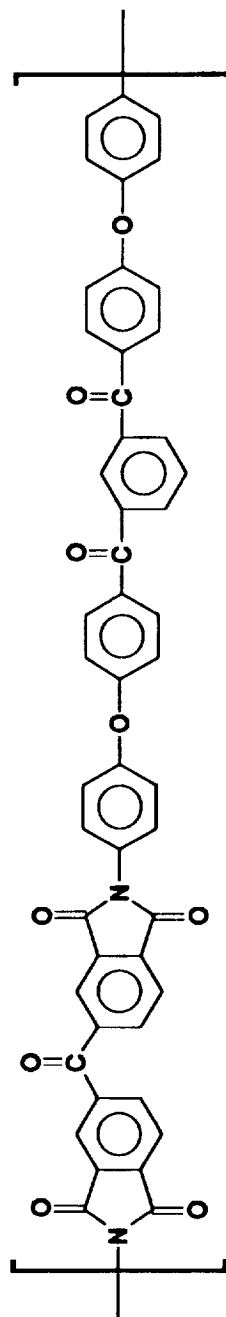


LARC-TPI

LARC-IA



LARC-ITPI



LARC-CPI

FIGURE 1 POLYIMIDE ADHESIVES

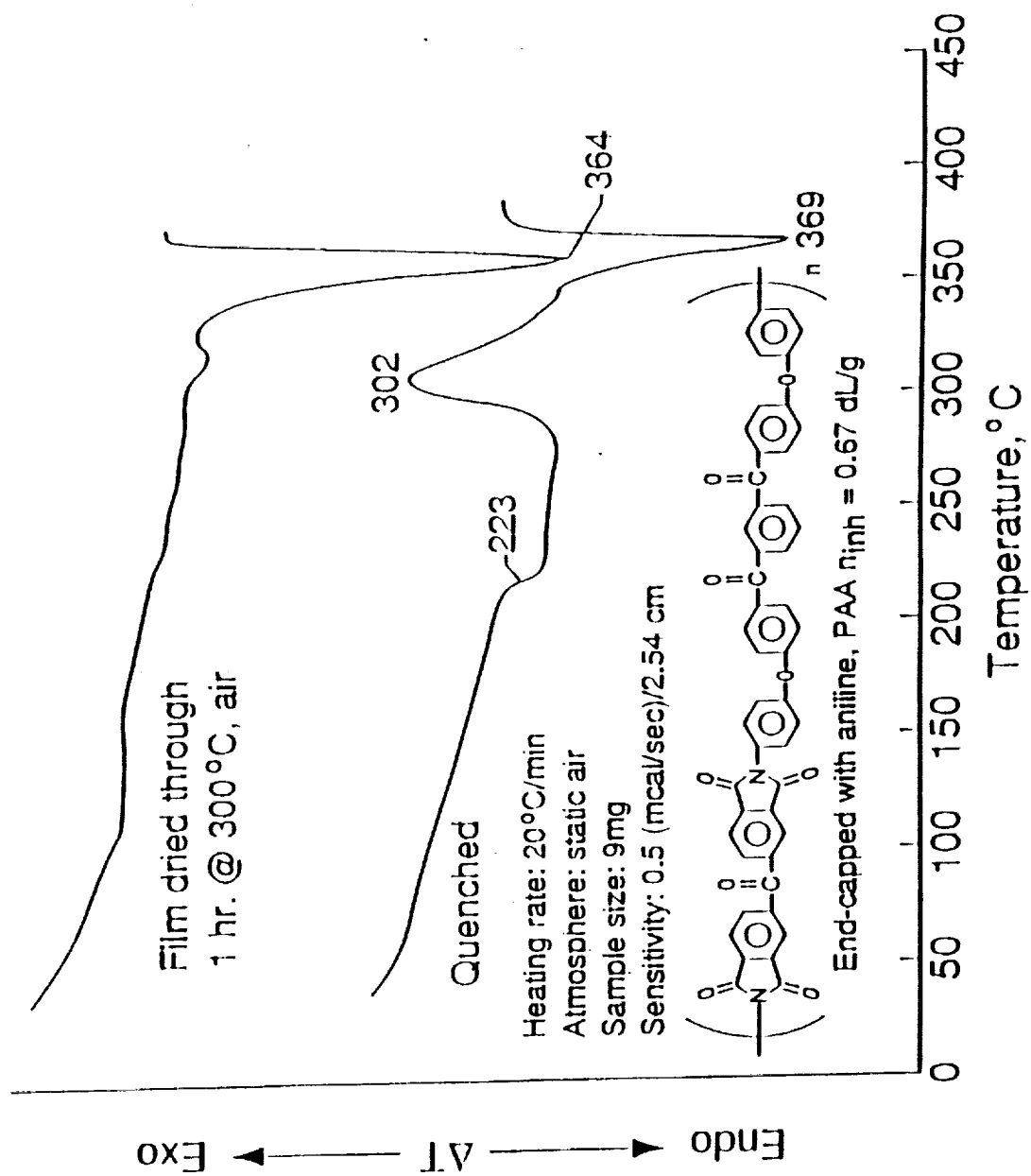


FIGURE 2 DIFFERENTIAL SCANNING CALORIMETRIC CURVES - LARC-CPI

TEST CONDITION	STRENGTH, PSI	FAILURE
25°C	6250	> 95% COHESIVE
25°C AFTER 3-DAY WATER BOIL	5140	~ 90% COHESIVE
25°C AFTER 72 HR HYDRAULIC FLUID SOAK	5590	~ 70% COHESIVE
25°C AFTER 1000 HR @ 232°C	7120	~ 100% COHESIVE
25°C AFTER 5 HR @ 300°C, 100 PSI	6130	> 95% COHESIVE
25°C AFTER 100 HR @ 316°C	4590	~ 70% COHESIVE
177°C	4510	> 95% COHESIVE
177°C AFTER 4 HR @ 300°C, 100 PSI	4690	~ 100% COHESIVE
232°C	590	~ 95% ADHESIVE
232°C AFTER 100 HR @ 232°C	1840	~ 50% COHESIVE
232°C AFTER 1000 HR @ 232°C	2740	~ 50% COHESIVE
232°C AFTER 5 HR @ 300°C, 100 PSI	2800	~ 80% COHESIVE
232°C AFTER 100 HR @ 316°C	3670	> 95% COHESIVE

*PASA-JELL 107 SURFACE TREATMENT; INHERENT VISCOSITY OF POLY(AMIC ACID) = 0.50 dL/g;
 BONDING CONDITIONS, 400°C, 1000 PSI, 15 MIN; 112 E-GLASS TAPE CONTAINED 0.1%
 VOLATILES, BONDLINE THICKNESS 5-6 MILS

FIGURE 3 LARC-CPI ADHESIVE DATA

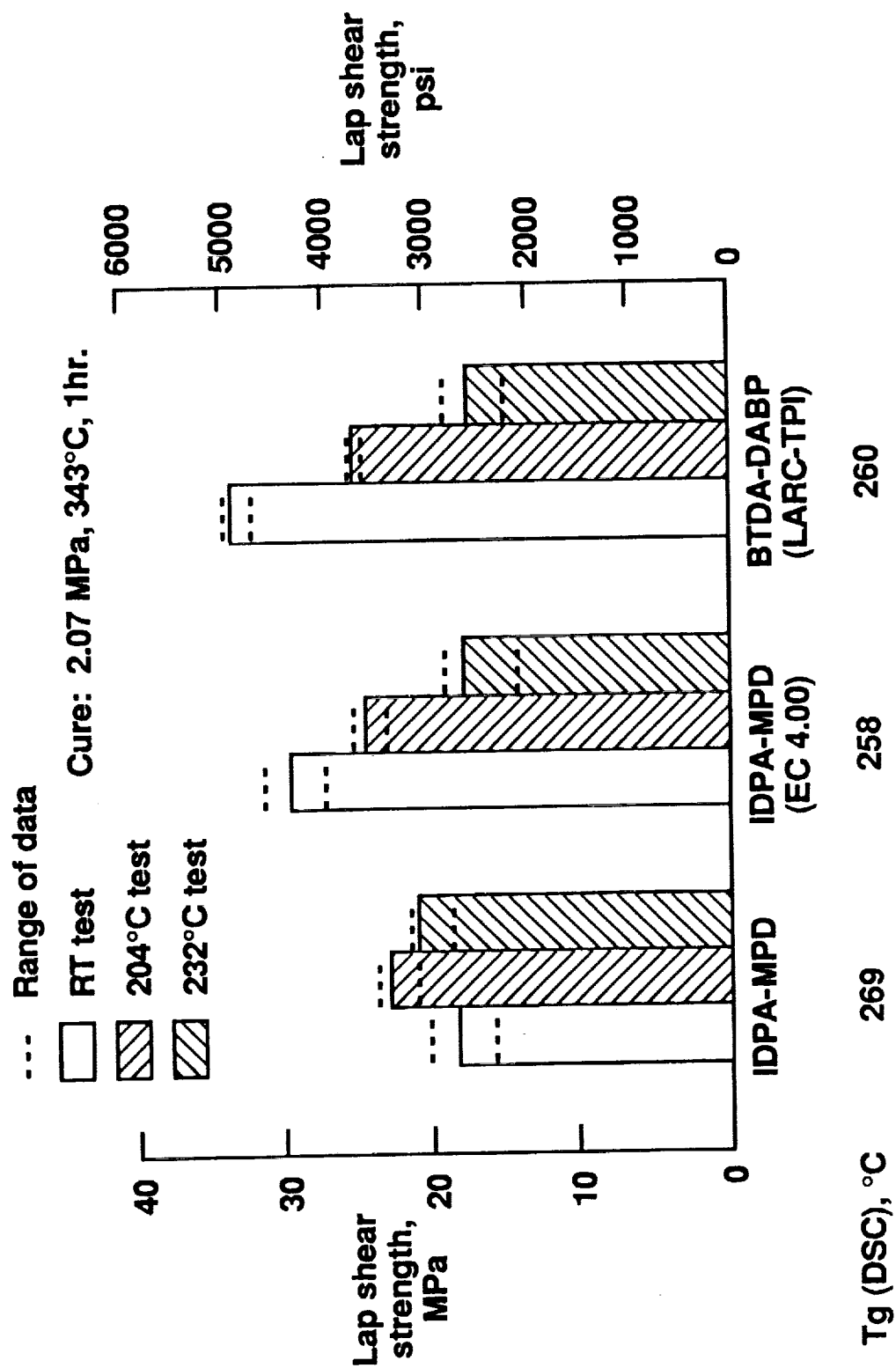


FIGURE 4 LARC-ITPI ADHESIVE DATA

Ti-6Al-4V Adherends

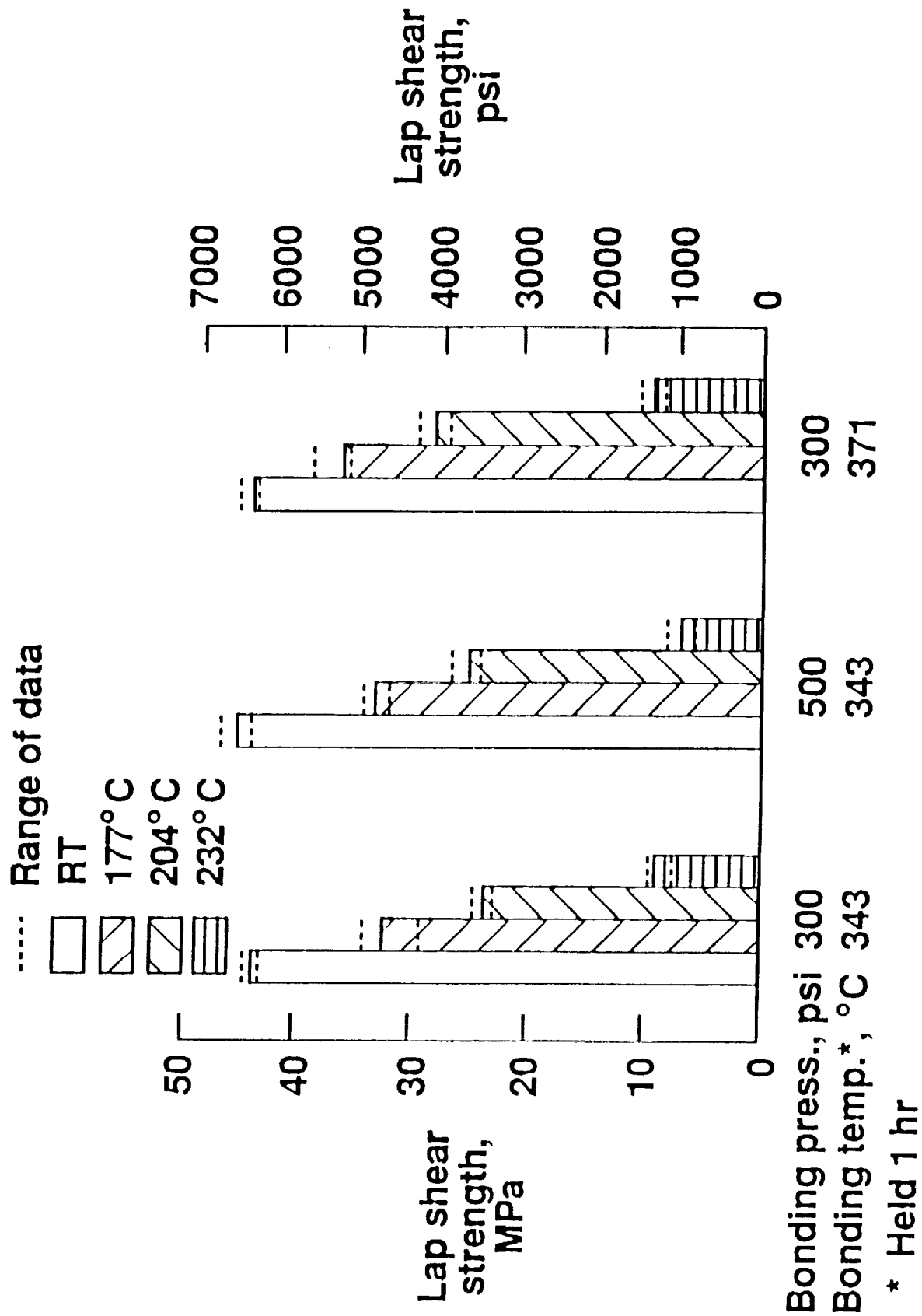


FIGURE 5 ADHESIVE DATA FOR LARC-IA

Adhesive	FWT ^a [MPa (psi)]	G _{1c} ^b $\left[\frac{\text{J}}{\text{m}^2} \left(\frac{\text{in. lb}}{\text{in.}^2} \right) \right]$
LARC-IA (5% PA)	1.7 (247)	560 (3.2)
	2.6 (378)	438 (2.5)
LARC-IA (5% PA) 50% Al powder	2.3 (340)	298 (1.7)
	2.4 (355)	210 (1.2)

^a Specimens were fabricated from Ti-6Al-4V facesheets [0.05 cm (0.020 in.)] and Ti core [0.95 cm (0.37 in.) cell size] given a Pasa Jell 107 surface treatment before priming and bonding

^b Specimens were fabricated from Ti-6Al-4V 0.13 cm (0.050 in.) thick and given a Pasa Jell 107 surface treatment before priming and bonding

FIGURE 6 FLATWISE TENSILE STRENGTH AND FRACTURE ENERGY FOR LARC-IA